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(54) Title: SPRAY CAST ALUMINIUM-LITHIUM ALLOYS

(57) Abstract

Aluminium-lithium alloys having reduced levels of impurities, particularly hydrogen and sodium and which exhibit improved mechanical properties.

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Spray Cast Aluminium-Lithium Alloys

This invention relates to aluminium-lithium based alloys having both low sodium and hydrogen contents and which are produced by spray deposition.

Aluminium-lithium based alloys are of great interest for applications requiring high stiffness with low weight,in particular for aerospace applications. However it is found that Al-Li alloys have relatively low ductility, fracture toughness and stress corrosion crack growth resistance in the short-transverse direction.

Kojima et al. (5th Int. Conf. on Al-Li alloys, AIME, p85, 1989) have examined the mechanical properties of spray cast aluminium-lithium 8090 alloy both as cast and following hot isostatic pressing. They report an apparent improvement in mechanical properties of spray cast alloy compared to values for DC cast 8090 alloy reported in the literature, although no direct comparison is made. The improved mechanical properties are attributed to a finer grain structure seen in the spray cast alloy.

Fager et al. (Scripta Metallurgica Vol. 20 p1159, 1986) have reported cleavage cracking in an Al-Li alloy. Sodium was indirectly identified as a possible embrittling agent together with potassium and titanium.

Miller et al. (Scripta Metallurgica Vol. 21, p663, 1987) have reported that cleavage cracking is not confined to Al-Li alloys. It was observed that provided the sodium content of the Al-Li alloy was

below approximately 10ppm the alloy did not exhibit cleavage cracking. The cleavage was believed to be due to sodium segregating to grain boundaries and particle matrix interfaces.

The effect of hydrogen content on mechanical properties of Al-Li alloys has not been quantified but circumstantial evidence suggests that hydrogen is detrimental.

The inventors have surprisingly discovered that aluminium alloys can be produced by spray deposition which have lower Na and H contents than those obtainable by conventional casting means and which show surprisingly good short-transverse mechanical properties after mechanical working. Accordingly in one aspect the present invention provides a method of reducing the volatiles content of aluminium alloys wherein a molten aluminium alloy containing volatile impurities is spray cast.

The term volatiles as used herein includes gaseous or high vapour pressure impurities for example hydrogen or alkali metals.

Preferably the melt is spray cast to form a coherent deposit. The method is particularly applicable to removal of Na and H_2 impurities.

The invention can be applied to the reduction of sodium and/or hydrogen content of any aluminium alloy. The method allows the sodium content of an aluminium alloy to be reduced without significantly altering the balance of other alloy components. The spray deposit may be remelted to provide a low sodium aluminium alloy feedstock or the spray deposit formed may be used directly or further worked before use.

The present invention is particularly applicable to aluminium-lithium based alloys, according to a further aspect of the invention there is provided a spray cast aluminium-lithium based alloy containing 2.5ppm or less of sodium and 1.0ppm or less of hydrogen.

The aluminium-lithium based alloys of the present invention may typically contain from 0.5 to 7% lithium, preferably from 2 to 6% lithium. The starting material from which the alloys of the present invention are produced may be a conventionally, DC cast aluminium lithium alloy or an alloy produced by another method. The sodium content of such DC cast alloys is generally around 10ppm typically 5ppm but may be as low as 3ppm. Preferably the sodium content of the starter alloy will be 10ppm or less.

Whilst it is recognised that sodium content of Al-Li alloys should desirably be below that at which the cleaveage type detect is observed, typically about 10ppm, the present inventors have found that by reducing sodium levels significantly below that at which sodium segregation occurs in combination with reduced hydrogen content the alloys exhibit surprisingly improved properties particularly in the short-transverse direction. Ductility and tensile strength are increased in both the long transverse and short transverse directions. The Fracture toughness is also increased in the short transverse direction. Resistance to stress corrosion crack growth and slow crack growth are substantially increased. Although mechanical properties in some areas, e.g. longitudinal direction, may be slightly reduced the alloys of the present invention show overall improved properties.

Aluminium-lithium based alloy of the present invention contains 2.5ppm or less Na and preferably 1ppm or less H_2.

Hydrogen content of DC cast Al-Li alloys is typically in the range 0.5-0.8ppm but may be as low as 0.3ppm. It is known that in high lithium alloys, typically those having a lithium content of 4% or greater, the hydrogen content is increased although the reason for this is not understood. For alloys having a Li content of 3% or less the H_2 content preferably does not exceed 0.3ppm and is preferably about 0.1ppm or less whereas for alloys with a lithium content of greater than 3%, H_2 content may be up to 1ppm but is preferably 0.8 ppm or less.

Alloys according to this invention may contain other elements (excluding Na and H_2) in proportion in which they are conventionally present in Al-Li alloys. Preferred alloys include 8090, 8091 series alloys. The invention covers both the alloy in the spray cast state and also products obtained by rolling, extrusion, forging, hot isostatic pressing or any other form of working. The purified alloy may also be remelted as a source of low impurity content material or recast.

A number of factors in the spray deposition process may influence the final sodium and hydrogen content of the sprayed ingot.

One factor which has an influence on the final sodium and hydrogen content is the crucible in which the melt is prepared. The crucible should preferably not be permeable to gases. The permeability of the crucible can allow a significant interaction

between the outside atmosphere (air) and the melt, thus leading to increased hydrogen levels. Preferred crucible materials include impermeable or semi-permeable materials such as resin bonded silicon carbide or bonded graphite crucibles. Other crucible materials include alumina, fused silica, magnesia and syalon and refractory lined steel crucibals. Impure refractories such as some types of alumina may react with the melt to increase sodium and hydrogen levels. To reduce this problem, the crucible may be treated with coatings such as boron nitride to inhibit reaction between melt and crucible and zirconia to reduce permeability. Other suitable coatings would be known to those skilled in the art.

The surface area to volume ratio of the bulk melt should be kept as low as possible (typically 0.015, preferably less than 0.038) in order to reduce the degree of interaction with the atmosphere. The atmosphere should be kept as dry as possible (typically < 10ppm and preferably < 6ppm of moisture) and hydrogen level as low as possible (typically < 10 ppm and preferably < 1 ppm) since water vapour is believed to be the major contributor to hydrogen level in the melt. The atmosphere should preferably also be inert to reduce oxidation. Vacuum melting has been found not to be necessary.

The removal of the volatile or gaseous impurities will be enhanced by atomizing to produce small particles (typically - 80μm, preferably < 200μm). However on reducing particle size the time of flight will be reduced resulting in less time for removal to occur. These two factors can be varied to optimize conditions to produce minimum sodium and

hydrogen levels in the deposit. If the particles were not deposited into a dense mass then the decreased gaseous impurity levels could not be retained in the solid state.

Degassing also occurs from the hot surface of the ingot when sprayed. This solid or semi-solid state degassing will be increased in deposits with greater thermal mass since heat is retained for longer.

In the following examples primary gas pressure was from 1.2 to 3 Bar, Secondary gas pressure from 5.5 to 9 Bar and transport gas pressure from 3 to 5 Bar. Primary gas flow rate was from 0.25 to $0.45m^3$/min, Secondary gas flow rate was from 6.0 to $9.2m^3$/min. Metal flow rate was from 5 to 14Kg/min. Melt temperature was from 700 to 800°C. Conditions were adjusted from within these ranges so as to produce metal particles which were liquid or semi liquid on impact and which had a diameter of less than 200µm. The above ranges may vary to some extent from one machine to another but suitable ranges to produce such particles can be readily determined.

By adjustment within the above ranges the particle size and flight time of particles may be optimized to achieve maximum removal of volatile impurities.

Example 1

Spray casting equipment was specified by Alcan International Limited and built by Mannesemann-Demag of West Germany and Osprey Metals, Neath and further developed at the Banbury Laboratories of Alcan International Limited. The alloy to be sprayed is

melted by induction heating in a Morgan "Salamander - Excel" crucible - Resin bonded SiC (40%, SiC and 30% carbon), the crucible being washed with a graphite/clay based wash and further coated with Boron Nitride. The equipment comprises a refractory nozzle for passing a stream of metal ejected using an overpressure. Surrounding the nozzle is a primary gas nozzle with apertures to direct a primary support gas flow parallel to and surrounding the metal stream to shroud and contain the molten metal. Surrounding the primary gas nozzle is a secondary gas nozzle provided with jets which direct a secondary atomizing gas stream towards the molten metal stream. The secondary gas stream contacts the molten metal stream at a distance downstream of the nozzle and atomizes it into a spray of metal particles.

The secondary atomizing gas flow defines a cone of height and radius equal to the distance of the jets from the metal stream.

The molten metal was sprayed onto a rotating aluminium alloy collector. The atomizing gas and transport gas used was nitrogen. The melt temperature was 710°C and total melting and holding time 3hr 50 min. The flow rate was 10.9 Kg/min and a spraying time of 8 min, 11 sec produced a spray deposit weighing 76.3 Kg.

The alloy sprayed was monolithic 8090 aluminium-lithium based alloy from DC cast starting stock. The properties of extrusions produced from the sprayed preform were compared to those of extrusions produced from DC cast starter billet. The preform was homogenised with a DC cast control for 24hrs at 550°C. The sprayed preform and DC cast billet were machined to 210mm diameter and extruded to a 2.5"X1" rectangular bar using the following parameters:

	Billet temp (°C)	Exit speed (M/min)	Exit Temp (°C) Front	Back
Spray	435/440	0.76	405	390
DC Cast	435/440	0.84	415	385

Extrusion ratio was 20:1 for both ingots. Suitable lengths were taken from the front and back of each extrusion for evaluation. The chemical analyses for these extrusions was as follows:

	Li	Cu	Mg	Zr	Si	Fe	Ti	Na	H_2
	(wt%)							ppm	
DC Cast	2.39	1.20	0.83	0.13	0.04	0.04	0.031	12	1.20
Spray	2.30	1.10	0.80	0.13	0.03	0.04	0.049	<1	0.19

The front sections of extrusions were then solution heat treated at 540°C for 1/2 hr, cold water quenched and 2% stretched.

Longitudinal, long-transverse and short-transverse tensiles, and ST-L toughness specimens were then aged for 48 hrs at 170°C. Tensile properties for sprayed and DC cast 8090 in all three orientations are given in the following table.

		DC Cast	Spray
Longitudinal - 0.2%	PS (MPa)	537	512
	TS (MPa)	572	550
	Elong (%)	4.7	5.1
Long Transverse - 0.2%	PS (MPa)	409	390
	TS (MPa)	443	487
	Elong (%)	0.7	8.5
Short Transverse - 0.2%	PS (MPa)	344	350
	TS (MPa)	356	485
	Elong (%)	0.4	8.4

The grain size taken from a longitudinal section in the sprayed 8090 is of the order of 15 microns by 250 microns, the DC cast 8090 was 30 microns by 1-2 mm. The equiaxed as sprayed grain size was 70 microns. The following table gives fracture toughness of DC cast and sprayed 8090 from 10 mm thick compact tension ST-L specimens.

I.D	Condition	K1c MPa m
DC Cast	24/170°C	14.21
DC Cast	48/170°C	14.38
Sprayed	24/170°C	25.25*
Sprayed	48/170°C	17.18

* Invalid test due to insufficient thickness, therefore Kq value quoted.

The stress corrosion crack growth rates and slow crack growth rates are shown in figures 1 and 2 respectively.

This improved combination mechanical properties results wholly or mainly from the reduced Na and H_2 contents of the spray cast product as compared to the DC cast product.

Example 2

In order to study the effect of sodium and hydrogen content on mechanical properties preforms of 8090 alloy with varying sodium and hydrogen content were produced. Apparatus was essentially similar to that previously described. The crucible was of a semi-permeable alumina/silica fibre type which was coated with zirconia and boron nitride. Melt temperature was 710°C.

The sodium content was varied by varying the sodium content in the starting ingot. Hydrogen content was varied by doping the atomizing gas with water vapour.

A further preform was produced using the apparatus as described in Example 1. Melt temperature was 710°C with a flow rate of 9.3Kg/min.

The preforms were machined to 28 mm thick rolling blocks and homogenized for 24 hrs at 540°C. The samples were rolled to 25 mm in thickness, reheating between each pass, solution heat treated at 530°C and aged for 24 hrs at 170°C and tested in the short transverse direction. The chemical composition of the rolled plate together with values for short-transverse elongation and fracture toughness are given in the following table.

	Li --wt%--	Na	H_2	% elongation	fracture toughness Kq (MPa.m1/2)
		----ppm----			
at					
1	2.31	5	0.57	0.62	19.6
2	2.34	22	0.33	1.00	17.8
3	2.51	13	0.44	0.87	17.4
4	2.31	6	0.41	1.82	23.0
5	2.24	1	0.28	6.14	27.2

The elongation and toughness are significantly increased in sample 5 produced according to the present invention compared to comparative samples 1 to 4.

Example 3

Preforms of 8090 alloy were spray cast as under conditions essentially as described in Example 2. The chemical composition of the alloy before spraying and the sprayed preform are given below.

	Si	Fe	Cu	Mg	B	Zr	Na --ppm--	Li
Before Spraying								
1	0.06	0.05	1.37	0.94	3	0.12	60	2.65
2	0.06	0.04	1.33	0.87	3	0.12	100	2.48
After Spraying								
1	0.06	0.05	1.24	0.88	3	0.12	13	2.51
2	0.07	0.04	1.32	0.83	3	0.12	22	2.34

All values given in wt% except Na - ppm.

Example 4

Melting and Holding Time	=	2 hrs, 50 mins
Flow Rate	=	8.85kg/min
Run Time	=	22 mins, 42 secs
Sprayform Wt.	=	152.7kg

Block 85mm thick was cut horizontally across the sprayform, homogenised 24 hrs at 550°C. This was cut to give a rolling block 130mm long x 90mm wide x 85mm thick. Material was rolled from 85mm down to 28mm thickness in 5 passes, at 540°C.

Composition

Starting Stock - 8091 alloy

Li%	Cu%	Mg%	Zr%	Si%	Fe%	Ti%	Na (ppm)	H_2 (ppm)
2.70	1.90	0.85	0.10	0.04	0.06	0.41	22	0.95

As Sprayed

Li%	Cu%	Mg%	Zr%	Si%	Fe%	Ti%	Na (ppm)	H_2 (ppm)
2.68	1.73	0.86	0.11	0.03	0.05	0.022	2	0.23

Material was cut from the centre of the as-rolled plate, and blanks for ST tensiles were S.H.T. at 545°C for 1 hr and the oil quenched. They were then aged for 48 hrs at 170°C, in the unstretched condition. Tensile properties were as follows:-

0.2% PS (MPa)	UTS (MPa)	Elongation (%)
376	456.9	1.5

Example 5

Results showing hydrogen reduction in 7000 series aluminium alloy.

The alloy was non-standard but had 5.0 - 70% zinc and 2.0 - 2.5% magnesium. Three spraying runs were carried out.

Run 1 - The starting metal had .29% H^2 and after spraying this fell to .09%.

Run 2 - The H^2 level fell from .46% to .20%.

Run 3 - The H^2 level fell from .32% to .17%.

In all cases spraying conditions were substantially the same as for the aluminium lithium alloy examples.

CLAIMS

1. Spray cast aluminium-lithium alloy containing 2.5ppm or less sodium and 1.0ppm or less hydrogen.

2. A spray cast aluminium-lithium alloy according to claim 1, wherein the lithium content is from 0.5 to 7%.

3. A spray cast aluminium-lithium alloy according to claim 2, wherein the lithium content is from 2 to 4%.

4. A spray cast aluminium-lithium alloy according to any one of claims 1 to 3, wherein the hydrogen content is 0.3ppm or less.

5. A spray cast aluminium-lithium alloy according to any of claims 1 to 4 wherein the alloy is an 8090 or 8091 series alloy.

6. A method of spray casting an aluminium alloy having reduced content of volatile impurities, wherein an aluminium alloy containing volatile impurities is spray cast under condition so as to produce particles which have a diameter of less than 200µm and which are liquid or semi-liquid on impact.

7. A method according to claim 6, wherein the primary gas pressure is from 1.2 to 3 Bar, secondary gas pressure is from 5.5 to 9 Bar and transport gas pressure from 3 to 5 Bar.

8. A method according to claim 6, wherein the primary gas flow rate is from 0.25 to 0.45m^3/min secondary gas flow is from 6 to 9.2m^3/min and metal flow rate is from 5 to 14Kg/min.

9. A method according to claims 8, wherein the volatiles are hydrogen.

10. A method according to claims 6 to 8, wherein the volatiles are alkali metal.

11. A method according to claim 10, wherein the alkali metal is sodium.

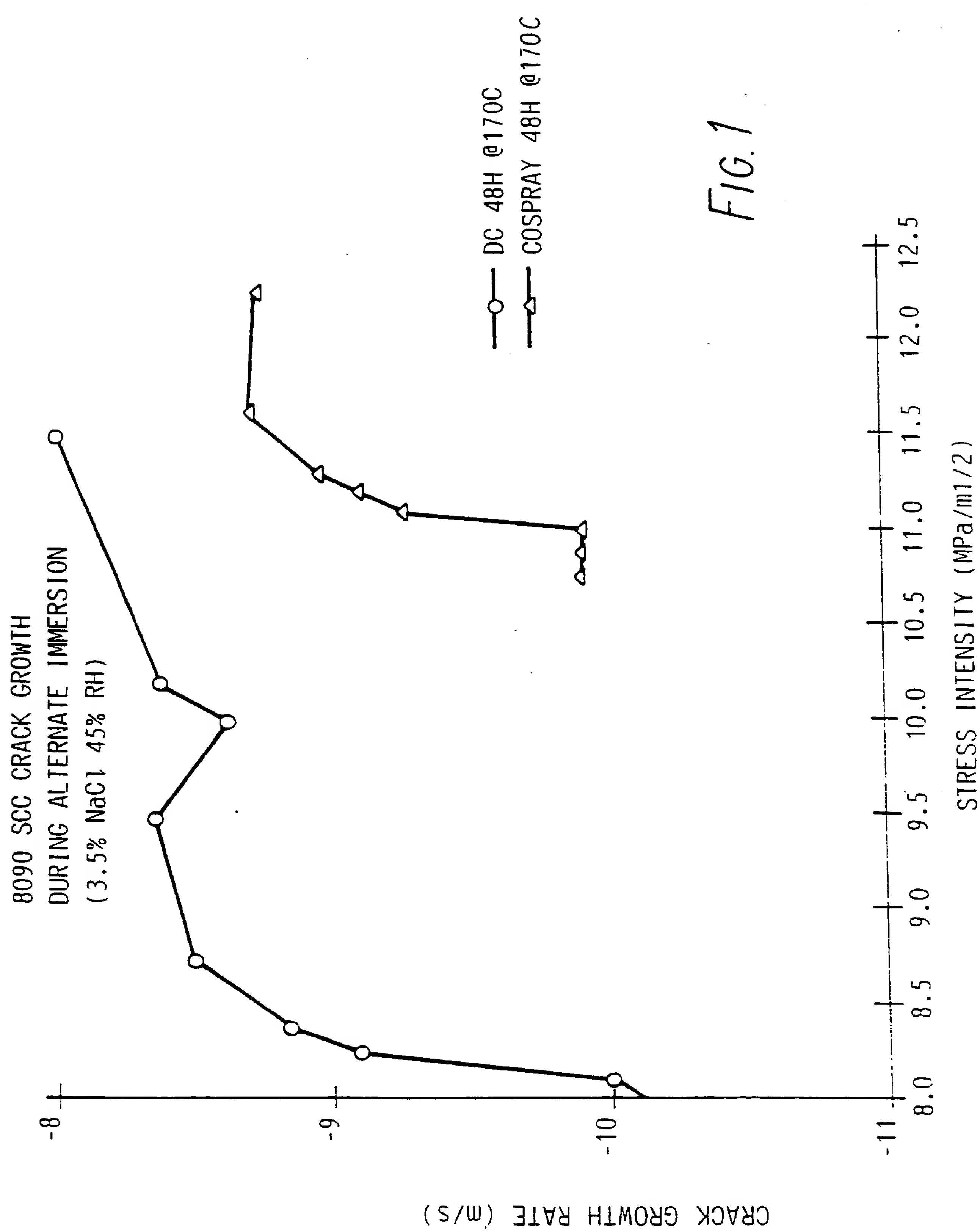
8090 SCC CRACK GROWTH
DURING ALTERNATE IMMERSION
(3.5% NaCl 45% RH)
DC 48H @170C
COSPRAY 48H @170C
CRACK GROWTH RATE (m/s)
-8
-9
-10
-11
STRESS INTENSITY (MPa/m1/2)
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
12.0
12.5

FIG. 1

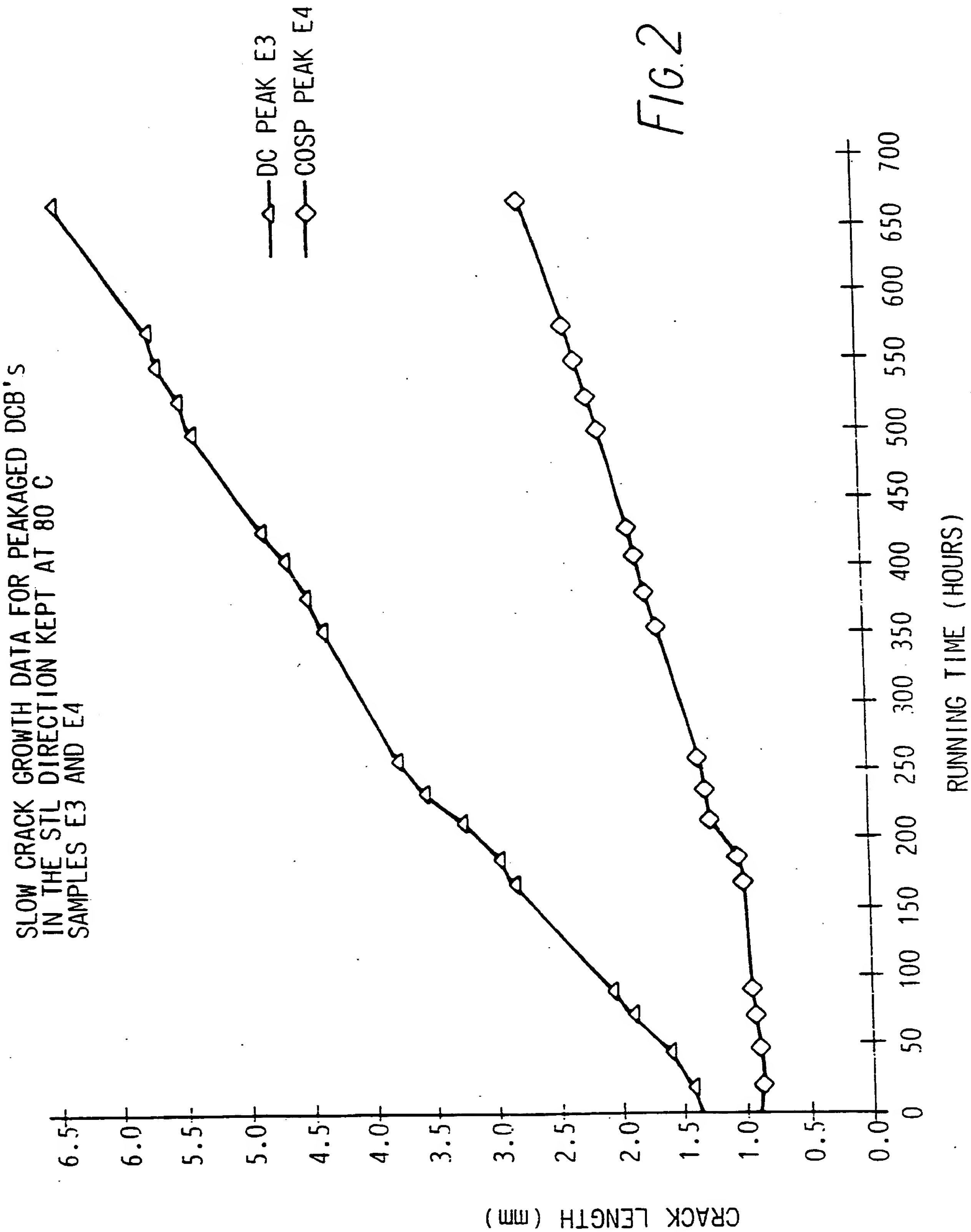
SLOW CRACK GROWTH DATA FOR PEAKAGED DCB'S
IN THE STL DIRECTION KEPT AT 80 C
SAMPLES E3 AND E4
DC PEAK E3
COSP PEAK E4
CRACK LENGTH (mm)
RUNNING TIME (HOURS)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
0
50
100
150
200
250
300
350
400
450
500
550
600
650
700

FIG. 2

ERNATIONAL SEARCH REPO

International Application No PCT/GB 91/00381

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC^5: C 22 C 1/02, C 22 C 21/00 // B 22 D 23/00 //

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC^5	C 22 C, C 23 C, B 22 D

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
A	US, A, 4049248 (O.G. GJOSTEEN et al.) 20 September 1977 see column 1, lines 12-16; examples 1-4; claim 1 ---	1,6
A	Aluminum - Lithium Alloys, Proceedings of the Fifth International Aluminum-Lithium Conference, Williamsburg, 27-31st March 1989, volume 1, MCEP, (Birmingham, GB), K.A. Kojima et al.: "Microstructural characterization and mechanical properties of a spray-cast Al-Li-Cu-Mg-Zr alloy", pages 85-91 see page 89, last paragraph; page 86, last two lines - page 87, first line; figure 1a cited in the application --- ./.	1,6

* Special categories of cited documents: [10]

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
30th May 1991	11. 07. 91
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	Natalie Weinberg

III. DOCUMENTS CONSIDERED TO BE RELEVANT (Continued from the second sheet)

Category*	Citation of Document with indication, where appropriate, of the relevant passages	Relevant to Claim N°
A	Metallurgical Transactions A, volume 18A, no. 12, December 1987, D. Webster: "The effect of low melting point impurities on the properties of aluminum-lithium alloys", pages 2181-2193 see abstract; table 1 ---	1-11
A	DE, B, 2043882 (VEREINIGTE ÖSTERREICHISCHE EISEN- UND STAHLWERKE AG), 11.March 1971 see claims 1,6,9; column 3, lines 49-51 ---	6
A	Scripta Metallurgica, volume 21, no. 5, 1987, Pergamon Journals Ltd., (US) W.S. Miller et al.: "Sodium induced cleavage fracture in high strength aluminium alloys", pages 663-668 see page 66, last paragraph cited in the application ---	1
A	Metallurgical Transactions B, volume 19B, April 1988, P.N. Anyalebechi et al.: "The solubility of hydrogen in liquid binary Al-Li alloys", pages 227-232 see page 227, left-hand column -----------	1,4

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. GB 9100381
SA 45325

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 28/06/91
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		AT-B- 331047	26-07-76
		AU-B- 473035	10-06-76
		AU-A- 4415772	14-02-74
		CA-A- 968166	27-05-75
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		FR-A- 2146767	02-03-73
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		DE-A,B,C 2043882	11-03-71

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82